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⑮ 反応装置

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明 細 書

1. 発明の名称

反応装置

2. 特許請求の範囲

一端に反応に供する流体入口をまた他端に反応生成物の流出口を設けた攪拌備付き反応容器において、該反応容器の内部壁上に付設された仕切り効果を有する静止型分散板によって該容器が複数のセルに分割されており各々のセルは同一の攪拌軸を共有して攪拌翼を備えていることを特徴とする気-液又は液-液反応装置。

3. 発明の詳細な説明

本発明は気-液又は液-液反応装置にかんし、とくに重合体の連続的改質反応装置にかんする。気-液反応系においては溶剤に溶解した状態の重合体と気体状の改質剤とを混合接触させて反応を行なわせ、液-液反応系では溶剤に溶解した状態の重合体と該重合体溶液よりも粘性の小さい液体状の改質剤とを混合接触させて反応を行なわせる。かかる気-液又は液-液反応系では均一で高

い反応率を達成するためには、改質剤を重合体溶液中に均一に微分散させ且つ反応器から排出される反応物の滞留時間分布を狭くする事が必要となる。一方化学工業分野では反応を均一に行わしめるために工夫をこらした反応装置が種々考案されている。例えば特開昭57-170914、同57-96006にみられる反応装置は混合すべき液体が高粘性液体状態では有効であるが気液反応系では気体成分の分散が不十分で効果は期待できない。また、特開昭57-125202で提案されている連続塊状重合反応装置は仕切型分散板を攪拌軸と共に回転させるため、邪魔板と反応容器壁との間に間隙を持たねばならない構造となっており、気-液反応系に用いると該間隙から気泡のショートパスが起こるため気泡を微分散させる事ができない。

本発明の目的は改質剤を含む流体を重合体溶液中に均一に微分散させ反応後の滞留時間分布を狭くさせ、従って均一で高い反応率を達成せしめる気-液又は液-液反応装置を提供することにある。

本発明に従って一端に反応に供する流体入口をまた他端に反応生成物の流出口を設けた攪拌機付き反応容器において、該反応容器の内部壁上に付設された仕切り効果を有する静止型分散板によって該容器が複数のセルに分割されており各々のセルは同一の攪拌軸を共有して攪拌翼を備えていることを特徴とする気-液又は液-液反応装置が提供される。

本発明の連続反応装置に適用できる重合体の改質反応例としては、

- (1) 天然ゴム、イソプレンゴム (IR)、エチレン-プロピレン-ジエンモノマー共重合体 (EPDM)、アクリルニトリル-ブタジエン共重合体 (NBR)、スチレン-ブタジエン共重合体 (SBR)、ブチルゴム (IIR)、ブロック SBR、アクリルゴム、ブタジエンゴム (BR) 等のゴム状重合体のフッ素、塩素、臭素、ヨウ素等の改質剤によるハロゲン化反応、
- (2) 同上ゴム状重合体の二酸化イオウ等の改質剤によるスルホン化反応、

に付設された仕切り効果を有する静止型分散板 5 によって 4 個のセルに分割されている。分散板 5 は攪拌軸 3 を間隙を以て圍繞する如く該軸の周りに開口部を形成している。

6, 7 は反応に供する流体入口で、8 は反応液流出口である。9, 10 は加熱あるいは冷却の出入口である。攪拌翼の回転方向は第 1 図あるいは第 2 図に示す如く翼が回転することによって液の流れが反応容器全体の液の流れ方向と逆になる様に回転させた方が、ショートパスを防ぎ、滞留時間分布を狭く、反応を均一にすることができるので好ましい。

攪拌翼については反応系の懸濁、粘性あるいは反応の性質により傾斜パドル翼、ディスクタービン翼、プロペラ翼等を使用できるが、第 2 図に示す如く傾斜パドルが好ましく特に 4 枚羽根の傾斜パドルが好ましいが、3 枚又は 2 枚羽根の傾斜パドル翼でもよい。傾斜パドル型攪拌翼の翼径 (d) については、反応容器内径 (D) に対して、その比が  $0.20 \leq d/D \leq 0.90$  になる様にするのが好まし

(3) 同上ゴム状重合体の水酸化反応、

(4) ポリエチレンの様な樹脂状重合体のハロゲン化、スルホン化あるいは水酸化反応

等があげられる。

これらの反応系は前述の様に気液系あるいは異粘性液-液系であるが、液-液系の場合乳化状態で行わせることも可能である。

また気-液反応系において不活性溶剤に溶解した重合体溶液と気体状の改質剤が反応器に供給されると直ちに強い攪拌力により改質剤の気泡が重合体溶液中に微分散し反応が開始する。この様に気泡が溶液中に微分散した状態が反応容器のどの部分に於ても形成、維持されながら全体としてはピストンフローに近い状態で反応物が反応器から排出される。

次に第 1 図に本発明の反応装置の一例を示す。図において 1 は円筒型の反応容器で、ジャケット 2 を備え必設に圧力、加熱若しくは冷却を行なう構造になっている。3 は攪拌軸で、これには攪拌翼 4 が取り付けられている。容器はその内部壁上

に、特に  $0.30 \leq d/D \leq 0.85$  が好ましい。d/D が 0.20 より小さい場合はセル内の流動が弱く特に気-液反応系では気泡の微分散が得られない。一方 d/D が 0.90 より大きくなると動力消費が大きくなり、気泡を微分散させるために高速度で攪拌翼を回転させることができなくなる。

攪拌翼巾 (b) と各セルの攪拌軸方向の長さ (L) との比は  $b/L \geq 0.20$  であるのが好ましい。b/L が 0.20 より小さくなると死空間的の滞留部分が生成し好ましくない。

傾斜パドル型攪拌翼の傾斜角度 ( $\theta$ ) は  $15^\circ \leq \theta \leq 70^\circ$  が好ましく、特に  $30^\circ \leq \theta \leq 60^\circ$  が好ましい。 $\theta$  が  $15^\circ$  より小さくなると反応器全体の液の流れ方向と同一の方向の液の流れが強くなり、ショートパスがふこりやすくなるので好ましくない。

一方  $\theta$  が  $70^\circ$  より大きくなると、攪拌が極めて弱くなり、気体の分散不良が起きるので、攪拌回転数を大巾に増大させなければならなくなる。

この様に回転数を大巾に増大させると攪拌軸の振れ、歪等が大きくなり、機械的損傷を招く結果

となるので好ましくない。

攪拌翼の回転数には特に制限はなく反応系の粘性、攪拌翼の径等を考慮し、適宜選定することが好ましいが、前述の如く、機械的損傷を招く程増大させるのは好ましくない。攪拌翼の径又は傾斜角度は全て同一とする必要はなく反応系の粘性に応じて適宜選定することができる。

本発明の装置においては、攪拌翼と攪拌翼の間に仕切り効果を有する分散板を静止させて設ける事によって、初めて次の効果が得られる。

- (1) 改質剤を含む流体が、重合体溶液中に、微細に分散するため、短かい反応時間で高い反応率が得られる。
- (2) 特に気液系では気泡が均一に微分散するため反応率の変動が極めて少なく反応を極めて安定に制御できる。
- (3) 反応器全体としてもピストンフローに近いため反応液の滞留時間分布が狭くなり、均一な組成を有する反応物を得る事ができる。
- (4) 少ない動力で所望の反応を行うことができ

行りに際し、重合体溶液の粘度は1~100,000センチポイズが適当で、特に1~30,000センチポイズが好適である。1センチポイズ以下の低粘度溶液には本装置をあえて用いる必要はなく、100,000センチポイズ以上の高粘度液に対しては本装置をもってしても改質剤の分散不良が起こり、本発明による以外の工夫が必要となる。

以上の様に、本発明によれば重合体の改質反応を行うに際して、少ない動力で、液体もしくは気体の状態の改質剤を重合体溶液中に均一に微分散させ、反応器全体としてピストンフローに近い極めて狭い滞留時間分布を有する連続反応装置が得られる。

又本発明の装置は一般の工業装置で使用されている攪拌翼である傾斜パドル等を使用できるという点で装置の製作も極めて簡単である。

又、本装置を用いると、高い反応率が得られる故、ハロゲン元素の様な毒性の極めて強い物質を重合体に付加させて重合体を改質させる場合、未反応のハロゲン元素の量が少なく、従って改質反

る。

前記の、仕切り効果を有する静止型分散板については、その開口面積比が攪拌軸に垂直な反応容器内断面面積に対し2~3%好ましくは3~15%の範囲に設定するのがよい。開口面積比が2%より小さくなると開口部での流速が大きくなり、重合体溶液を送り込むのに多大の動力を必要とするので好ましくない。又、30%を越すと、隣接セル間の液の移動が多くなり、仕切り効果が小さくなる。

ここで分散板の開口面積比とは分散板上に設けた複数の貫通孔の面積と分散板と攪拌軸との間隙部面積との合計開口面積と攪拌軸に垂直な反応容器断面面積との比を意味する。

分散板上に設けた複数の貫通孔の形状はとくに限定されないが、円形、楕円形、十字形あるいはスリット状が例示される。また分散板と攪拌軸との間隙部については、その開口面積は出来る限り小さい方が好ましい。

本発明による反応装置を用いて連続改質反応を

応以後の下流工程における中和等の後処理が極めて容易に行え、従って後処理も簡便なもので済むという利点を有する。

これらの点から、本発明は汎用性が広く、明細書中の実施例に限定されるものではなく、特許請求の範囲に記載された内容を満たす装置はすべて本発明に包含されるものである。

例えば、反応に供する流体を入口に最も近いセルのサイドから供給してもよいし、他のセルのサイドから種々の添加剤を供給することもできる。

尚、本発明で反応率とは、ゴム状重合体に結合した改質剤の量の、反応に供した改質剤の量に対する割合で表わされる値である。

以下に実施例を示す。

#### 実施例1

市販のEPDM(エチレンプロピレンターポリマー)であるJSR EP57( $ML_{1+4}^{100C} = 90$ 、プロピレン含量28重量%、炭素価15.0)をn-ヘキサンに溶解した固形分濃度10.0重量%の重合体溶液を予め調製しておいた。次にこの重合体溶液を

120 l/HR ( EPDM 8.2 kg/HR ) で、本発明で用いる反応容器に供給すると同時に、塩素ガスを179 Nl/HR ( 8.0 mole/HR ) で該反応容器に供給し、EPDMの塩素化を連続的に行わしめた。反応圧力、温度、攪拌の回転数をそれぞれ0.5 kg/cm<sup>2</sup>G、80℃、140 rpmに一定に制御し反応を継続した。

反応容器としては本発明による第1図で示した円筒型反応容器を使用した。

この反応容器は内径350 mm、長さ750 mmでジャケット及び液出入口を備えている。

この反応容器には中心に攪拌軸がついており、その攪拌軸には4個の、傾斜角度45°の4枚傾斜パドル型攪拌翼及びそれらの攪拌翼の間に、攪拌軸周りの開口部の形状が円形である円板状の多孔型分散板が容器内壁に付設されており反応容器内が4個のセルに分割されている。傾斜パドルの大きさは真径280 mm、真幅75 mmのものを用いた。

攪拌翼の向きはすべて同一方向で回転方向は第1図の様になる方向である。

板と反応容器の内壁の間に3 mm巾の間隙を設けた。分散板は開口面積比が実施例1と同じになるように5 mm径の孔の数を減少させた多孔性分散板を用いた。反応が定常に達した後5分毎に分析した塩素含量を第3図に示した。

塩素の反応率は平均で49%であった。又除害処理に必要とした水酸化ナトリウムは6.7 mole/HRであった。

#### 比較例2

実施例1と同じ条件であるが、反応器での傾斜パドル型攪拌翼のかわりに真幅35 mm、真軸長150 mm、翼の外径330 mmの半ピッチ2重らせん型攪拌翼を用い、且つ、攪拌軸と共に回転する分散板を攪拌翼と攪拌翼の間に取り付け、EPDMの塩素化反応を行った。この分散板は比較例1で用いたものを使用した。反応が定常に達した後5分毎に分析した塩素含量を第3図に示した。塩素の反応率は平均で30%であった。

#### 実施例2

ポリイソブレンゴムを四塩化炭素に溶解した固

又、円板状の多孔板は厚さ3 mmで直径5 mmの孔が軸を中心放射線状に12方向に計300個設けられている。(開口面積比6.6%)

この様な反応容器を用いてEPDMの塩素化反応を行わしめた。

反応が定常に達した後、反応容器出口の配管中から塩素化されたEPDMを5分毎に採取し、洗浄処理を施し、しかる後溶剤を除去乾燥し結合した塩素の含量を元素分析法で測定した。塩素含量は第3図に示す如く極めて良好に制御されていることが判った。

尚、塩素の反応率は平均で76%であった。

次に、反応器から排出される液中に水酸化ナトリウム水溶液を添加し、未反応の塩素及び副成する塩化水素を除去し、除害処理を行った。除害処理に必要とした水酸化ナトリウムは2.3 mole/HRであった。

#### 比較例1

実施例1と同じ条件でEPDMの塩素化を行ったが分散板を攪拌軸と共に回転する様にとりつけ分散

形分濃度5.0重量パーセントのゴム状重合体溶液を予め調製しておいた。次にこのポリイソブレンゴム溶液を、ポリイソブレンゴムとして2.8 kg/HRの割合で実施例1と同じ反応容器に供給すると同時に塩素ガスを3,490 Nl/HR ( 156 mole/HR ) で該反応器に供給しポリイソブレンゴムの塩素化反応を連続的に行わしめた。

反応圧力、温度、攪拌の回転数はそれぞれ1.0 kg/cm<sup>2</sup>G、80℃、140 rpmの値に一定に制御し、反応を継続した。

反応が定常に達した後、反応容器出口の配管中から塩素化されたポリイソブレンゴムを5分毎に採取し、洗浄処理を施し、しかる後溶剤を除去、乾燥し、塩素含量を測定した。塩素含量は第4図に示す如く極めて良好に制御されていることが判明した。塩素の反応率は平均で47%であった。

#### 比較例3

実施例2と同じ条件でポリイソブレンゴムの塩素化を行ったが実施例2で用いた反応容器の分散板を全て取り除き、仕切りをなくした形に変えた

反応容器を用いた。

反応が定常に達した後5分毎に分析した塩素含量を第4図に示した。

塩素の反応率は平均で20%であった。

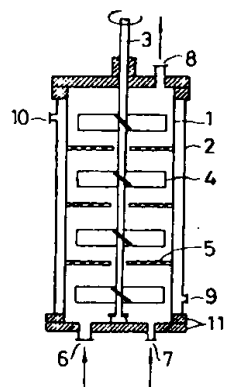
4. 図面の簡単な説明

第1図は本発明の反応装置を示し、第2図は傾斜パドル式攪拌機を用いた反応容器内のセル構造を示す。

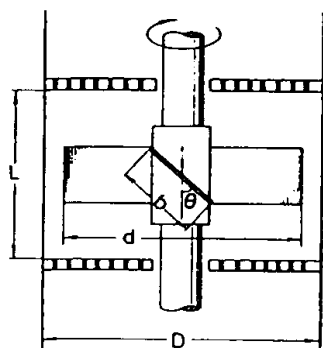
- 1：反応容器本体、2：ジャケット、3：攪拌軸、4：攪拌翼、5：静止型分散板、6：反応に供する流体入口、7：反応に供する流体入口、8：反応物出口、9：熱媒もしくは冷媒入口、10：熱媒もしくは冷媒出口、11：フランジ、

第3図及び第4図は塩素化反応における塩素含有量の時間的推移を示すグラフである。

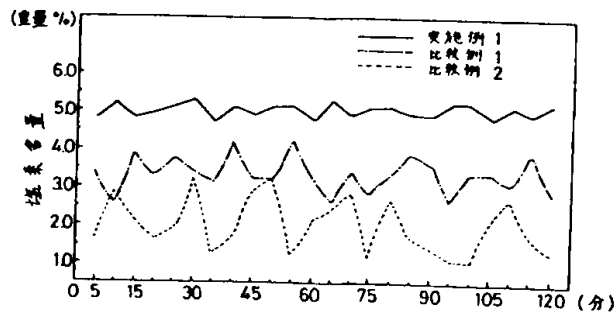
第 1 図



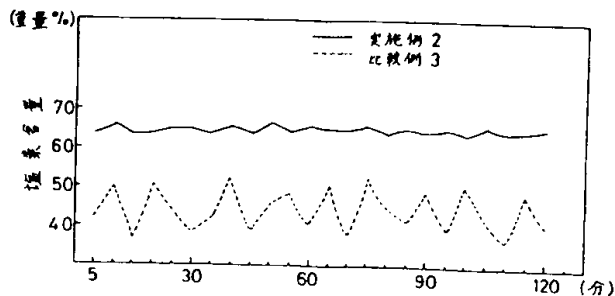
第 2 図



第 3 図



第 4 図



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10

(54) Reaction Apparatus

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### Specification

30 1. Title of the Invention

Reaction Apparatus

2. Patent Claim

35 A gas/liquid or liquid/liquid reaction apparatus characterized in that, in a reaction container with a stirrer that is provided on one end with a fluid inlet port for the reaction, and on the other end with an outflow port for the produced reaction fluid, the reaction container is separated into a plurality of cells by stationary dispersion plates having a partitioning effect attached to an inner wall of the reaction container, the various cells sharing the same agitator shaft and being provided  
40 with agitator blades.

3. Detailed Description of the Invention

The present invention relates to gas/liquid and liquid/liquid reaction apparatuses, and in particular to apparatuses for continuous modification reaction of polymers.

45 In Gas/liquid reaction systems, a polymer that has been dissolved in a solvent is mixed and brought into contact with a gaseous modifier to perform the reaction, and in liquid/liquid reaction systems,

a polymer that has been dissolved in a solvent is mixed and brought into contact with a liquid modifier with lower viscosity than the polymer solution to perform the reaction. In order to attain a uniform and high reaction rate in such gas/liquid and liquid/liquid reaction systems, it is  
5 necessary to finely disperse the modifier uniformly throughout the polymer solution and to narrow the distribution of residence times of the reaction product discharged from the reaction vessel. In the field of chemical industry, various reaction apparatuses have been proposed that are designed to let the reaction be carried out uniformly. For  
10 example, the reaction apparatuses disclosed in JP 57-170914A and JP 57-96006A are effective when the liquids to be mixed are highly viscous, but in gas/liquid reaction systems, the gas component is insufficiently dispersed, so that no effect can be expected. Furthermore, in the continuous bulk polymerization reaction apparatus proposed in JP 57-  
15 125202A, partition-type baffle plates are rotated together with an agitator shaft, so that the structure is such that a gap must be kept between the baffle plates and the reaction container walls, and when a gas/liquid reaction system is used, bubbles may pass directly through the gap, so that fine dispersion of the bubbles is not possible.

20 It is an object of the present invention to provide a gas/liquid or liquid/liquid reaction apparatus, in which a fluid containing modifier can be uniformly and finely dispersed in a polymer solution, the distribution of residence times of the reaction liquid can be narrowed, and consequently, a uniform and high reaction ratio can be attained.

25 The present invention thus presents a gas/liquid or liquid/liquid reaction apparatus characterized in that, in a reaction container with a stirrer that is provided on one end with a fluid inlet port for the reaction, and on the other end with an outflow port for the produced reaction fluid, the reaction container is separated into a plurality of cells  
30 by stationary dispersion plates having a partitioning effect attached to an inner wall of the reaction container, the various cells sharing the same agitator shaft and being provided with agitator blades.

35 Examples of the polymer modification reactions to which the continuous reaction apparatus of the present invention can be applied include:

(1) halogenation reactions of rubber polymers such as natural rubber, isoprene rubber (IR), ethylene-propylene-dienemonomer copolymer (EPDM), acrylonitrile butadiene copolymer (NBR), styrene-butadiene copolymer (SBR), butyl rubber (IIR), block SBR, acryl rubber,  
40 or butadiene rubber (BR), with modifiers such as fluorine, chlorine, bromine or iodine.

(2) sulfonation reactions of the above-noted rubber polymers with modifiers such as sulfur dioxide,

(3) hydrogenation reactions of the above-noted rubber polymers,  
45 (4) halogenation, sulfonation and hydrogenation reactions of resinous polymers such as polyethylene.

These reaction systems are gas/liquid systems or liquid/liquid systems with different viscosities as described above, but in the case of liquid/liquid systems, it is also possible to carry out the reaction in an emulsified state.

5 As for gas/liquid reaction systems, when a polymer solution dissolved in an inert solvent and a gaseous modifier are supplied into a reaction vessel, a strong stirring force is applied immediately, bubbles of the modifier are finely dispersed throughout the polymer solution, and the reaction begins. Thus, while a state in which the bubbles are finely  
10 dispersed throughout the solution spreads to and is maintained in all portions of the reaction container, the reaction product is discharged from the container in a state that is overall close to a piston flow.

Fig. 1 shows an example of a reaction container of the present invention. In this figure, 1 is a cylindrical reaction container, that has a jacket 2 and can be heated or cooled, as necessary. 3 is an agitator shaft to which agitator blades 4 are attached. The container is divided  
15 into four cells by stationary dispersion plates 5 that are attached to an inner wall of the container and have a partitioning effect. The dispersion plates 5 leave a gap to the agitator shaft 3 and, surrounding the shaft, form an aperture portion around it.  
20

6 and 7 are inflow ports for the reaction, and 8 is a reaction liquid outflow port. 9 and 10 are the inlet and outlet ports for the heating or cooling medium. It is preferable that the rotation direction of the agitator blades is such that it causes the flow direction of the liquid  
25 to be opposite to the flow direction of the liquid in the entire reaction vessel, as shown in Fig. 1 and Fig. 2, because this prevents direct passing through, the distribution of residence times can be made narrow, and the reaction can be made uniform.

For the agitator blades it is possible to use for example inclined  
30 paddle blades, disk turbine blades, or propeller blades, depending on the type of the reaction system, the viscosity, and the nature of the reaction, but as shown in Fig. 2, inclined paddles are preferable. Four-winged inclined paddles are particularly preferable, but three-winged or two-winged inclined paddles are also acceptable. It is preferable that  
35 the ratio between the blade diameter (d) of the inclined paddle agitator blades and the internal diameter (D) of the reaction vessel is  $0.20 \cdot d/D \cdot 0.90$ .  $0.30 \cdot d/D \cdot 0.85$  are particularly preferable. If  $d/D$  is smaller than 0.20, then the flow in the cells becomes too weak, and particularly in gas/liquid reaction systems, fine dispersion of the  
40 bubbles cannot be attained. On the other hand, if  $d/D$  is larger than 0.90, then the power consumption becomes large, and it becomes impossible to rotate the agitator blades at high speed in order to finely disperse the bubbles.

It is preferable that the ratio between the agitator blade width (b) and the length (L) of the cells in the direction of the agitator shaft is  $b/L \cdot 0.20$ . When  $b/L$  is smaller than 0.20, then dead-space-like residence  
45



portions develop, which is undesirable.

It is preferable that the inclination angle ( $\theta$ ) of the inclined paddle agitator blades is  $15^\circ < \theta < 70^\circ$ .  $30^\circ < \theta < 60^\circ$  are particularly preferable. When  $\theta$  is smaller than  $15^\circ$ , then the flow of the liquid in the direction of the flow of the liquid in the overall reaction vessel becomes weak, so that direct passing through tends to occur, which is undesirable.

On the other hand, if  $\theta$  is larger than  $70^\circ$ , then the agitation becomes extremely weak, and the dispersion of gas becomes inferior, so that the revolving speed of the stirring has to be increased considerably.

When the revolving speed is increased considerably, oscillations and warping of the agitator shaft increases, which may lead to mechanical defects and is thus undesirable.

There is not particular limitation regarding the revolving speed of the agitator blades, and it should be chosen as appropriate in consideration of the viscosity of the reaction system, the diameter of the agitator blades, etc. As mentioned above, it is not preferable to increase the revolving speed to a level that may entail mechanical defects. It is not necessary to make the diameters and the inclination angles of the agitator blades all identical, and they can be chosen as appropriate in accordance with the viscosity of the reaction system.

In the apparatus of the present invention, the following novel effects are attained by providing stationary dispersion plates having a partitioning effect between the agitator blades:

(1) The fluid including the modifier is finely dispersed within the polymer solution, so that a high reaction rate can be attained in a short reaction time.

(2) In particular in gas/liquid systems, the bubbles are uniformly and finely dispersed, so that variations in the reaction rate are extremely small, and the reaction can be regulated to be extremely stable.

(3) The entire reaction vessel is close to a piston flow, so that the residence time distribution of the reaction liquid is narrow, and reaction products having a uniform composition can be attained.

(4) The desired reaction can be carried out with little motive power.

The aperture/area ratio of these stationary dispersion plates having a partitioning effect to the cross-sectional area within the reaction container perpendicular to the agitator shaft should be set to a range of 2 to 3%<sup>1</sup>, preferably 3 to 15%. If the aperture/area ratio is less than 2%, then the flow speed at the aperture portions becomes large, and a very large motive power becomes necessary in order to feed the polymer solution forward, which is undesirable. If it exceeds 30%, then too much liquid shifts between neighboring cells, and the partitioning effect is diminished.

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<sup>1</sup> Translator's Note: Possibly a mistake for "2 to 30%"

Here, aperture/area ratio of the dispersion plates means the ratio of the total aperture area, including the area of the plurality of through holes provided in the dispersion plates and the area of the gap portion between the dispersion plates and the agitator shaft, with  
5 respect to the cross-sectional area of the reaction container perpendicular to the agitator shaft.

There is no particular limitation regarding the shape of the plurality of through holes provided in the dispersion plates, and they can be circular, elliptical, cross-shaped or slit-shaped, for example. It is  
10 preferable that the aperture area of the gap portion between the dispersion plates and the agitator shaft is as small as possible.

For performing a continuous modification reaction using the reaction apparatus of the present invention, a viscosity of the polymer solution of 1 to 100,000 centipoise is suitable, and particularly 1 to  
15 30,000 centipoise are preferable. For low viscosity solutions of less than 1 centipoise, it is not necessary to use the apparatus of the present invention, and for high viscosity solutions of more than 100,000 centipoise, the dispersion of the modifier will be inferior even with the apparatus of the present invention, and other measures in addition to  
20 the present invention will be necessary.

Thus, with the present invention, for performing a polymer modification reaction, a continuous reaction apparatus is attained, with which a modifier in form of a liquid or a gas can be uniformly and finely dispersed throughout the polymer solution with little motive force, and  
25 in which the overall reaction vessel has an extremely narrow residence time distribution that is close to piston flow.

Furthermore, making the apparatus of the present invention is very simple regarding the fact that for the agitator blades, inclined paddles or the like can be used, which are commonly used in industrial  
30 apparatuses.

Furthermore, since a high reaction rate can be attained when using the apparatus of the present invention, when a polymer is modified by adding a substance with extremely high toxicity, such as halogens, the amount of unreacted halogens is small, and consequently  
35 there is the advantage that after-processing such as neutralization in a step downstream from the modification reaction is extremely easy, so that after-processing is easy.

In these regards, the present invention has great versatility and is not limited to the embodiment in this specification, and all apparatuses fulfilling the conditions noted in the patent claims are encompassed in the present invention.  
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For example, the fluid that is introduced for the reaction can be supplied from the side of the cell that is closest to the inlet port, but it is also possible to supply various additives from the side of other cells.  
45

It should be noted that in the present invention, reaction rate is the value expressed by the proportion of the amount of modifier that

has bonded with the rubber polymer to the amount of modifier given to the reaction.

The following is an explanation of working examples.

5 Working Example 1

10 A polymer solution with a solid compound concentration of 10.0 wt% was prepared by dissolving JSR EP57 ( $ML^{100^\circ C}_{1+4}=90$ , propylene content 28 wt%, iodine value 15.0), which is a commercial EPDM (ethylene propylene terpolymer) in low hexane. Then, this polymer solution was supplied to a reaction container of the present invention at 120 l/hr (EPDM 8.2 kg/hr) while at the same time supplying chlorine gas at 179 Nl/hr (8.9 mol/hr) to the reaction container, and chlorination of EPDM was performed continuously. The reaction was sustained, regulating the reaction pressure, temperature and stirrer revolving speed to constant values of 0.5 kg/cm<sup>2</sup>G, 80°C and 140 rpm, respectively.

For the reaction container, a cylindrical reaction container according to the present invention as shown in Fig. 1 was used.

20 This reaction container has an inner diameter of 350 mm, a length of 750 mm, and is provided with a jacket and liquid inlet/outlet ports.

25 The reaction container has an agitator shaft, which is provided with four inclined paddle agitator blades with an inclination angle of 45°, and between these agitator blades, disk-shaped perforated dispersion plates with a circular aperture portion around the agitator shaft are attached to the inner walls of the container, dividing the inside of the reaction container into four cells. The size of the inclination paddles was 280 mm blade diameter and 75 mm blade width.

30 The orientation of the agitator blades is the same for all blades and the rotation direction is as shown in Fig. 1.

Furthermore, the thickness of the disk-shaped perforated plate is 3 mm, and a total of 300 holes with 5 m diameter are provided radially fanning out in 12 directions from the shaft (aperture/area ratio: 6.6%).

35 Using such a reaction container, the EPDM chlorination reaction was carried out.

40 After the reaction has reached constancy, the chlorinated EPDM was collected every 5 minutes from the tubing of the reaction container outlet port, subjected to a rinsing process, and then, the solvent was eliminated, the EPDM was dried, and the content of the attached chlorine was measured by elemental analysis. As shown in Fig. 3, it was found that the chlorine content is regulated extremely favorably.

It should be noted that the reaction rate of the chlorine was 76% on average.

45 Next, an aqueous solution of sodium hydroxide was added to the liquid discharged from the reaction vessel, and unreacted chlorine as

well as hydrogen chloride were removed in an elimination process. The sodium hydroxide necessary for the elimination process was 2.3 mol/hr.

5 Comparative Example 1

Chlorination of EPDM was performed under the same conditions as in Working Example 1, but a gap of 3 mm width was provided between the dispersion plates and the inner walls of the reaction container, so that the dispersion plates rotated together with the  
10 agitator shaft. For the dispersion plates, perforated dispersion plates were used in which the number of holes of 5 mm diameter was reduced so that the aperture/area ratio was the same as in Embodiment 1. Fig. 3 shows the chlorine content, analyzed every 5 minutes after the reaction reached constancy.

15 The reaction rate of the chlorine was 49% on average. Furthermore, the sodium hydroxide necessary for the elimination process was 6.7 mol/hr.

Comparative Example 2

20 The conditions were the same as in Embodiment 1, but instead of the inclined paddle agitator blades of the reaction vessel, half-pitch double-helix band agitator blades with a blade width of 35 mm, a blade shaft length of 150 mm and an outer blade diameter of 330 mm were used, and dispersion plates rotating together with the agitator shaft  
25 were attached between the agitator blades, and then the EPDM chlorination reaction was performed. For the dispersion plates, the plates used in Comparative Example 1 were used. Fig. 3 shows the chlorine content, analyzed every 5 minutes after the reaction reached constancy. The reaction rate of the chlorine was 30% on average.

30 Working Example 2

A rubber polymer solution with a solid component concentration of 5.0 wt% was prepared by dissolving polyisoprene rubber in carbon tetrachloride. Then, this polyisoprene rubber solution was supplied to  
35 the same container as in Working Example 1 at a proportion of 2.8 kg/hr while at the same time supplying chlorine gas at 3,490 Nl/hr (156 mol/hr) to the reaction vessel, and a chlorination reaction of polyisoprene rubber was performed continuously.

The reaction was sustained, regulating the reaction pressure, temperature and stirrer revolving speed to constant values of 1.0  
40 kg/cm<sup>2</sup>G, 80°C and 140 rpm, respectively.

After the reaction has reached constancy, the chlorinated polyisoprene rubber was collected every 5 minutes from the tubing of the reaction container outlet port, subjected to a rinsing process, and  
45 then, the solvent was eliminated, the polyisoprene rubber was dried, and the chlorine content was measured. As shown in Fig. 4, it was

found that the chlorine content is regulated extremely favorably. The reaction rate of the chlorine was 47% on average.

### Comparative Example 3

5        The chlorination of polyisoprene rubber was performed under the same conditions as in Working Example 2, but all dispersion plates of the reaction container used in Working Example 2 were removed, and the reaction container was used without the dispersion plates.

10       Fig. 4 shows the chlorine content, analyzed every 5 minutes after the reaction reached constancy.

         The reaction rate of the chlorine was 20% on average.

### 4. Brief Description of the Drawings

15       Fig. 1 shows a reaction apparatus in accordance with the present invention. Fig. 2 shows the cell configuration within a reaction container using inclined paddle agitator blades.

20       1: reaction container unit, 2: jacket, 3: agitator shaft, 4: agitator blades, 5: stationary dispersion plates, 6: inflow port for the reaction, 7: inflow port for the reaction, 8: reaction product outlet port, 9: heating medium or cooling medium inlet port, 10: heating medium or cooling medium outlet port, 11: flange,

         Fig. 3 and Fig. 4 are graphs showing the chlorine content over time in a chlorination reaction.

Drawings:

Fig. 3

vertical axis: chlorine content (in wt%)

horizontal axis: (min)

- 5
- \_\_\_\_\_ Working Example 1
  - . - . - . - Comparative Example 1
  - - - - - Comparative Example 2

10 Fig. 4

vertical axis: chlorine content (in wt%)

horizontal axis: (min)

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- \_\_\_\_\_ Working Example 2
  - - - - - Comparative Example 3

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